

Adsorption-Induced Solvent-Based Electrostatic Gating of Charge Transport through Molecular Junctions

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Recent experiments have shown that transport properties of molecular-scale devices can be reversibly altered by the surrounding solvent. Here, we use a combination of first-principles calculations and experiment to explain this change in transport properties through a shift in the local electrostatic potential at the junction caused by nearby conducting and solvent molecules chemically bound to the electrodes. This effect is found to alter the conductance of 4,4'-bipyridine-gold junctions by more than 50%. Moreover, we develop a general electrostatic model that quantitatively predicts the relationship between conductance and the binding energies and dipoles of the solvent and conducting molecules. Our work shows that solvent-induced effects are a viable route for controlling charge and energy transport at molecular-scale interfaces.

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Single-molecule junctions, individual molecules contacted with macroscopic electrodes, provide unique insight into the nanoscale physics of charge, spin, and energy transport [1–4]. To date, the most robust and reproducible approach to assemble single-molecule junctions is the scanning tunneling microscope-based break junction (STM-BJ) technique [5, 6], allowing statistically significant measurements of molecular junction conductance [5–9], thermopower [10–12], mechanical properties [13–15], and binding mechanisms [15]. Previously-developed theoretical approaches have led to quantitative agreement with experiment for molecular junctions, given a good approximation to the junction geometry and a good estimate of the differences in energy ΔE between the junction Fermi energy, E_F and the orbital energy of the frontier orbital, either the highest occupied or lowest unoccupied molecular orbital (HOMO or LUMO, respectively) [16]. Theoretical works focusing on this level alignment [17, 18] have led to increased understanding and control of molecular junction conductance and thermopower in terms of junction level alignment, with significant impact on experiments [10–12, 19].

Commonly, these experiments take place at room temperature in a non-conductive solvent [5–8], which has recently been shown to influence both junction formation probability and, in some cases, to alter the conductance [20]. Despite its practical importance, the impact of these solvents on conductance has not yet been fully understood or explained by theory, in part due to the large computation cost [21], and, therefore, continues to be elusive to control. Previous theoretical works have focused on the effect of solvent on the average [22, 23] and dynamical [24] molecular junction geometries, and how they affect level alignment and modify the conductance [25]. Another focus has been the coupling of transmission channels due to intermolecular

hopping between conducting molecules [26], in the case solvent would influence the formation of multiple simultaneous junctions. However a detailed physical picture and quantitative framework for understanding how solvent affects junction level alignment remains elusive despite clear evidence [20]: new theory and models are required to understand and better control solvent effects on junction transport properties. Given the significant recent interest in solvent-base gating of correlated oxides [27], graphene [28], and transition metal dichalcogenides [29], such a theory will have general implications.

In this Letter, we explain the effect of solvent on molecular device transport properties in a manner analogous to a chemical electrostatic gate controllably altering the local potential of the junction. We demonstrate how the electrode surface can act as a template to order the adsorbate molecules near the junction, resulting in large, ordered induced dipoles and a sizable, coherent shift of the average junction electrostatic potential, outweighing bulk effects associated with thermal fluctuations at room temperature and the low intrinsic dipole moment of the unbound solvent molecules. This picture arises out of our explicit quantitative theoretical calculations of the effects of the molecular coverage, θ , on the transport properties of 4,4' bipyridine-gold (Au-BP-Au) junctions comparing directly with new experimental data. For Au-BP-Au junctions, we accomplish this by taking advantage of the periodic boundary conditions in our transport calculation by changing the cross-section of the supercell - see Figure 1(a) - and find that a high molecular coverage results in conductance values per molecule one and a half times larger than those in the dilute limit. This effect originates from the coverage dependence of the local potential at the junction [30], which acts as a local electrostatic gate and alters junction level alignment. We further introduce a model that, in combination with first-

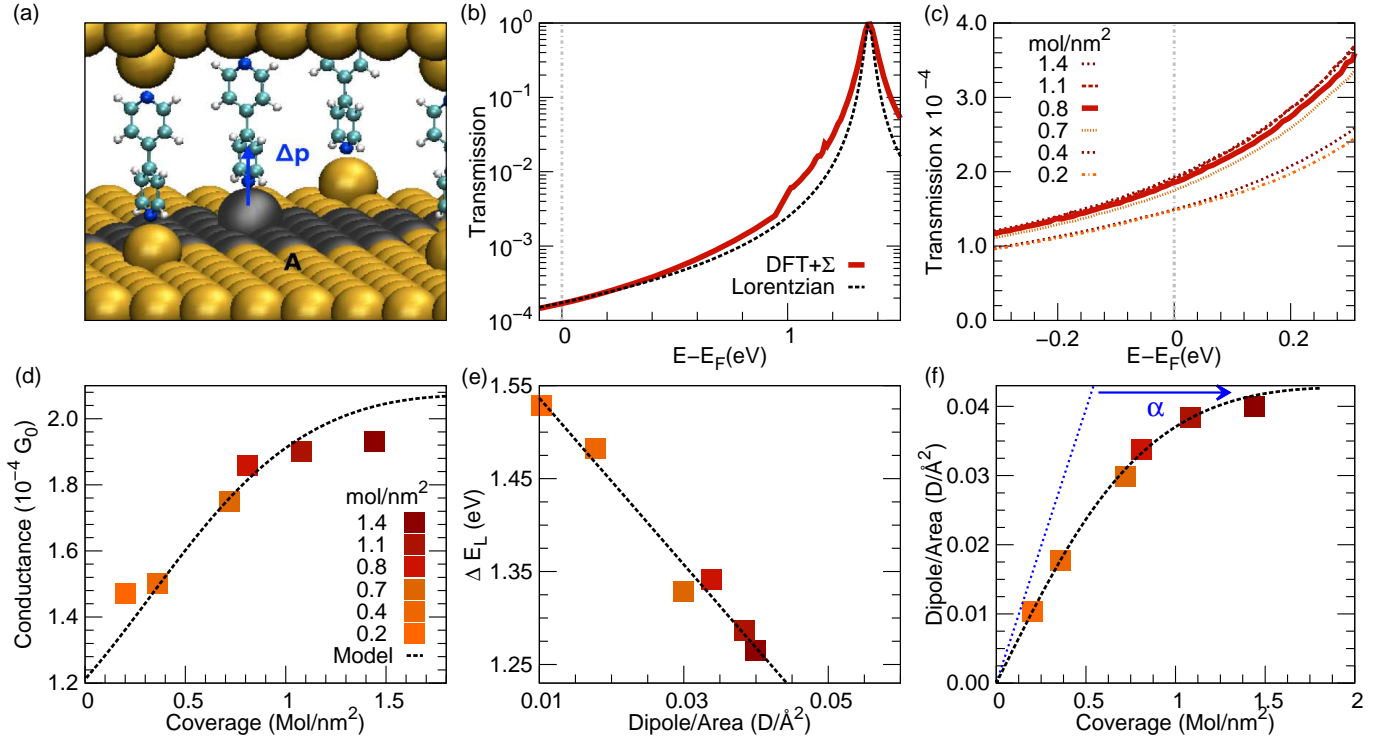


FIG. 1: (a) Junction geometry for 0.8 molecule/nm² coverage with periodic boundary conditions used in transmission calculations. Cross-sectional area indicated with a black shadow, and the induced dipole with a blue arrow. (b) Transmission function of Au-BP-Au junction at a 0.8 molecule/nm² coverage with Lorentzian fit. (c) The transmission function of Au-BP-Au junctions for different coverages ranging 0.2-1.4 molecule/nm² near E_F . (d) The DFT+ Σ conductance of Au-BP-Au compared to a electrostatic based model as a function of coverage. (e) The linear dependence of level alignment on dipole/area. (f) The nonlinear dependence of dipole/area on coverage: this is due to depolarization of the polarizable interface dipoles, black line from model, blue is the case without depolarization.

principles calculations, explains the experiments quantitatively for arbitrary surface concentrations of solvent and conducting molecules and predicts that the conductance of HOMO- and LUMO- conducting molecular junctions exhibits an opposite trend in solvent- dependence, demonstrating the potential for different solvents to discriminate between hole or electron transport, much like a thermopower measurement. The magnitude of these effects is comparable to the one induced by ionic gating [31], establishing liquid neutral solvents as a potential route to realize three-terminal device physics in single-molecular junctions.

We optimize junction geometries using density functional theory (DFT) within the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [32, 33] using the SIESTA code [34, 35]. Each gold lead is modeled with six (111) layers, where the three outer layers of each are constrained to the bulk geometry and the cross-section of gold atoms in the lead supercell ranges from 3x3 to 8x8. The Au-BP-Au junction geometry used in the calculation, as shown in Figure 1(a), is

similar to previous work [36]. Our transport calculations are carried out within an *ab initio* Landauer framework using a scattering state method implemented in the Scarlet code [37], with an in-plane k -mesh of 16x16 for the 4x4 cross-section and is adjusted accordingly for other junctions. In order to correct the Kohn-Sham DFT-PBE energy level alignment for missing exchange and correlation effects, we apply an approximate GW correction within the DFT+ Σ framework [38, 39] (All details of calculations given in Supp. Mat.). We find the Au-BP-Au junction LUMO resonance energy by diagonalizing the junction Hamiltonian projected on the molecular subspace and the dipole per area (areal dipole) is calculated by integrating the first moment of the DFT-PBE electronic density on one side of the center of charge of the junction, making use of its near-inversion symmetry. To isolate the induced areal dipole upon binding, Δp , the areal dipoles of the isolated gold electrode and molecule are subtracted from that of the junction; see Figure 1(a).

The results of our calculations are summarized in Figure 1. Figure 1(b) shows the DFT+ Σ transmission func-

tion, $T(E)$, near the E_F , which is dominated by single LUMO resonance and has a Lorentzian lineshape: $T(E) = \Gamma^2/(\Gamma^2 + 4(\Delta E_L - E)^2)$, where Γ is the full width half maximum ($\Gamma = 0.036$ eV, see Supp. Mat.) and $\Delta E_L \sim 1.3$ eV is the LUMO resonance peak energy relative to E_F . This agrees with previous experimental and theoretical works on the Lorentzian lineshape of the transmission function of Au-BP-Au junctions [12, 16, 36, 40, 41]. Upon variation of the molecular coverage over from 0.2 to 1.4 molecule/nm², the predicted conductance ranges from $1.47 - 1.93 \times 10^{-4} G_0$, shown in Figure 1(c), where the conductance $G = G_0 T(E_F)$ and $G_0 = 2e^2/h$, and furthermore is shown to vary nonlinearly - see Figure 1(d). This significant variation is not a consequence of intermolecular coupling [26], as at full molecular coverage the in-plane dispersion of the LUMO in momentum space is 0.007 eV, accounting for less than a 1% spread in conductance. Instead, the coverage alters conductance much in the manner adsorbates on a surface alter the work function [42].

As we will now demonstrate, the variation in conductance comes from a shift of the local potential. The change in local potential upon coverage can be observed in the variation of the LUMO resonance energy as shown in Figure 1(e). As BP and the solvent in this work are neutral species, the local potential varies at first order as the function of the areal dipole $\Delta p/A$ of the system. As shown in Figure 1(e), this truncation of the local potential at the dipole term is in excellent agreement with the DFT+ Σ calculations, *i.e* the LUMO resonance energy, ΔE_L , as a function of coverage is:

$$\Delta E_L \left(\frac{\Delta p}{A} \right) = \Delta E_L^{\theta \rightarrow 0} - \eta \frac{\Delta p}{A}. \quad (1)$$

The position of the LUMO resonance in the infinitely dilute limit is $\Delta E_L^{\theta \rightarrow 0} = 1.63$ eV and the slope is $\eta = 8.95$ eV·Å²/D. The slope of this line is less than one expects from Poisson's equation, $\sim 12\pi$ in these units (See Supp. Mat.), as the two sides of the junction are close enough to interact with each other effectively allowing the gold leads to heavily screen the electrostatic interactions in the junction. We note that the areal dipole does not vary linearly with molecular coverage due to significant depolarization effects [42, 43], as shown in Figure 1(f).

To gain further quantitative insight into the dependence of Δp on coverage, we develop a lattice model of point-polarizable dipoles induced by binding events for both slab and junction geometries. Assuming flat electrodes in the vicinity of the junction, the model is comprised of two infinite planar interfaces on either side of the conducting molecule of length d , one at $z = 0$ and the other at $z = d$. Each interface has an array of dipoles, Δp , pointing towards the center of the junction on a regular rectangular lattice, with spacing corresponding to a given molecular coverage; see the inset of Figure 2. The interface dipole induced by molecular binding (on either

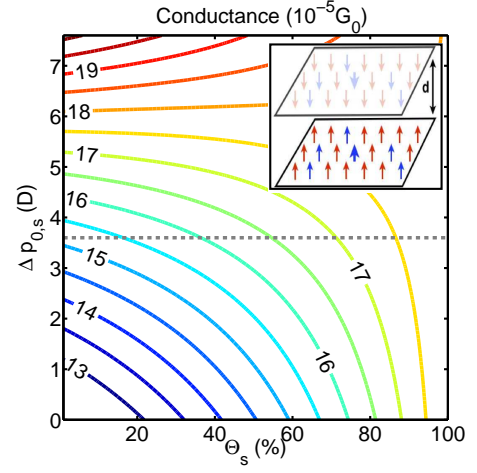


FIG. 2: The conductance, given by the electrostatic model, as a function of the ratio of BP molecules to solvent on surface concentration, Θ_s and dipole of bound solvent with a molecular coverage of 0.8 molecule/nm². Grey dashed line denotes dipole of trichlorobenzene (TCB). Inset: Schematic of dipole lattice model with 30% surface concentration of conducting molecule (blue) in solvent (red). The larger arrows denote the molecule bridging the interfaces.

side) can be considered as a bare dipole, Δp_0 , with polarizability, α , which depolarizes due to the collective electric field of all other dipoles, and which we express as

$$\Delta p(\theta, d) = \frac{\Delta p_0}{1 + \alpha k(\theta, d) \theta^{3/2}}. \quad (2)$$

where $k(\theta, d)$ is a coverage-dependent sum over purely geometric factors (see Supp. Mat.), following Topping [44]. To fit α and Δp_0 we use Eq. (2) in the one-interface limit: $d \rightarrow \infty$ and the induced areal dipoles from DFT calculations of BP-Au slabs at various θ . Subsequently, d is fit by using Eq. (2) in the case of finite d and induced areal dipoles from the corresponding DFT calculations of Au-BP-Au junctions. For the case of BP we find $\alpha_{BP} = 97$ Å³, $\Delta p_{0,BP} = 7.6$ D and $d = 7.31$ Å. Combining Eqs. (1) and (2), we complete our description of how level alignment varies with coverage. Assuming a Lorentzian limit for the conductance, which is valid for Au-BP-Au junctions, we can use this description of level alignment as a function of coverage to and model conductance as a function of coverage as

$$G(\theta) = \frac{2e^2}{h} \frac{\Gamma^2}{\Gamma^2 + 4 \left(\Delta E_L^{\theta \rightarrow 0} - \eta \theta \frac{\Delta p_0}{1 + \alpha k \theta^{3/2}} \right)^2}. \quad (3)$$

This model shows excellent agreement to the first-principles calculations in Figure 1(d) for Au-BP-Au junctions.

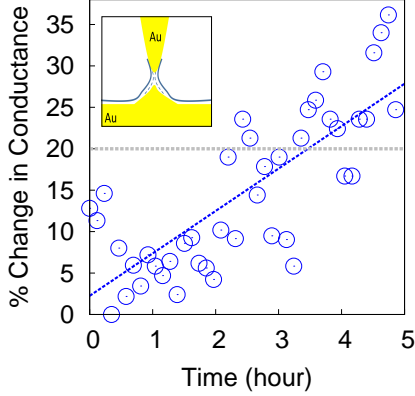


FIG. 3: Time resolved percentage change in conductance of Au-BP-Au STM BJ in TCB over 5 hours. As the solvent evaporates the solution becomes more concentrated, and the conductance increases. Comparison to maximal change in model shown in grey, inset: cartoon of experiment.

To incorporate the effects of solvent, we allow for two species of dipoles in our model: one representing the bound solvent molecule and the other the bound conducting molecule; see inset of Figure 2. The polarizability, α_s , and bare dipole, $\Delta p_{0,s}$, of the bound solvent are calculated, as for the conducting molecule, by fitting the dipole from solvent on gold DFT calculations at various θ to the one interface depolarization expression - Eq. (2). Breaking our infinite planar interfaces into large supercells of N sites, we construct a random configuration of the two-dipole species with a specified surface concentration of BP molecules to solvent molecule: Θ_s . The depolarization of the N dipoles can be written as a system of equations; *i.e.*,

$$\Delta p_i = \Delta p_{0,i} - \alpha_i \sum_{j=1}^N \Delta p_j k(\theta, d, r_{ij}) \theta^{3/2}, \quad (4)$$

where $i = 1, \dots, N$, and $k(\theta, d, r_{ij})$ is again dependent on geometric factors: θ is the density of available binding sites and r_{ij} is the relative displacement between Δp_i and Δp_j . Upon solving this system of equations, we calculate the average areal dipole per supercell, $\Delta \tilde{p}(\Theta_s)$, and can generalize Eq. (3) by replacing the depolarized dipole as expressed in Eq. (2) with $\Delta \tilde{p}(\Theta_s)$.

Figure 2 shows the results of our model for conductance as we vary $\Delta p_{0,s}$ and Θ_s , using parameter for BP and $\alpha_s = 55 \text{ \AA}^3$, assuming a density of 0.8 available binding sites/nm². For $\Delta p_{0,s} = 0$ we recover our single dipole case with BP at various coverages. We note that in the case of high solvent molecule coverage, and a large solvent-induced dipole relative to the conducting molecule, we can, in principle, use this “solvent gate” to achieve a higher conductance than for a coverage of only

conducting molecules; however, such a situation would result in low junction formation probability in the corresponding STM-BJ experiment. These shifts in conductance, due to collective surface effects, outweigh any contribution from the bulk solvent as it is not ordered: any ordering of the solvent, with an intrinsic dipole of the order of $\simeq 1$ D in the presence of an electric field resulting from experimental bias of $\simeq 1$ MV/cm are washed out by fluctuations at room temperature. Moreover, the induced dipole upon binding is larger than the intrinsic dipole: 0 D vs. 7.6 D for BP and 2.5 D vs. 3.6 D for TCB. Only the molecules on the surface contribute to the junction potential: the surface templates their dipoles, leading to a coherent, collective effect. For experiments done at a lower temperature, higher bias, or with a solvent with a much higher intrinsic dipole, such bulk effects would be expected to begin to play an appreciable role, a subject for future study.

Finally, we support our theory with time-dependent conductance measurements of Au-BP-Au junctions, in the presence of TCB solvent (details in Supp. Mat.). We compare the percent change in conductance for $\Delta p_{0,s} = 3.6$ D the dipole of TCB bound to gold to the percent change in conductance for BP on gold in a 0.01 mM solution of TCB over 5 hours. Over the course of the experiment the TCB evaporates and the concentration of BP in the vicinity of the junction increases, resulting in an increased conductance. As shown in Figure 3, we observe a variation of 20% in conductance from our model ($1.5 \times 10^{-4} G_0 - 1.8 \times 10^{-4} G_0$) and a variation of $37 \pm 12\%$ in the experiment ($8.7 \times 10^{-5} G_0 - 1.11 \times 10^{-4} G_0$). The overall absolute difference between experiment and theory can be attributed to the flat electrodes in the model and the lack of binding site variation, as we have assumed all adatom binding sites: by varying the binding site for a molecular coverage of 0.8 mol/nm², we find a conductance of $1.8 \times 10^{-4} G_0$ for adatom-adatom, $1.2 \times 10^{-4} G_0$ for adatom-trimer, and $9.6 \times 10^{-5} G_0$ for trimer-trimer.

In summary, we developed a quantitative understanding and general model of the effects of the solvent environment on the conductance of single-molecule junctions, and performed accompanying measurements. Our model predicts a significant shift in conductance for the specific case of Au-BP-Au junctions, with a magnitude and sign comparing very well with experiment. This solvent-induced electrostatic gating effect – at its core – is due to the solvent and conducting molecules bound to the surface at the vicinity of the junction, which changes the local electrostatic potential. We demonstrate that an electrostatic model approximating the junction and its surroundings by an array of point-polarizable dipoles quantitatively captures these effects and can be extended to incorporate the effect of nearby solvent molecules on the local potential and conductance, acting as a local gate. The magnitude of these reversible effects establishes liquid neutral solvents as a potential route to real-

ize three-terminal device physics in single-molecular junctions. Our model and findings are general, and can be applied to arbitrary surface concentrations of solvent and conducting molecules, and is thus useful for predictive design of future multiterminal nanoscale transport devices.

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